

Title: New York State Electric & Gas Corporation's Utility  
Experience with Sulfur Trioxide and Sulfuric Acid Mist

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The presence of sulfur trioxide ( $\text{SO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) mist in utility fossil-fired flue gas streams contributes to the corrosion of power plant equipment and increased visual plume opacity. This presentation will discuss case histories detailing the findings of investigative studies and solutions implemented to reduce  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  mist from the flue gas emissions of several coal-fired electric generating facilities owned and operated by New York State Electric and Gas Corporation (NYSEG).

NYSEG's Hickling and Jennison generating stations consist of a total of eight stoker-fired boilers with a combined capacity of 151 MW. The boiler flues are paired up for a total of four operating stacks, two at each station. Following the implementation of particulate emission standards, all eight boilers were retrofitted with electrostatic precipitators in the early 1970's to control visible opacity and particulate emissions. A longstanding problem at these stations has been the formation of a detached blue colored plume in the flue gas emitted from all four stacks.

Flue gas sampling and analysis at Hickling Station identified  $\text{SO}_3$  as the likely cause of the plume opacity. The injection of a sodium aluminate solution into the flue gas upstream of the economizer was implemented to correct the problem. This additive was successful in reducing the plume opacity, but hindered the performance of the precipitators and was not economically acceptable. Ammonia injection systems were then installed at both Hickling and Jennison to reduce the  $\text{SO}_3$  and sulfuric acid emissions contributing to the opacity. Ammonia injection upstream of the precipitator was proven effective in reducing the flue gas sulfur trioxide concentration and did reduce the stack opacity. However, ammonia injection was not totally effective in eliminating the blue condition altogether. Higher than acceptable plume visibility persisted, although at a lower frequency than before ammonia injection began. The frequency and intensity of the plume opacity continued to be highly variable.

In 1994, a flue gas sampling and analysis program was undertaken on Hickling Station's Boiler No. 1. The purpose of this study was to follow the progress of  $\text{SO}_3$  formation and removal from the combustion products as flue gas traveled from the furnace to the stack, to locate the regions in which  $\text{SO}_3$  formation and removal were most rapid, and to identify the conditions influencing the emissions of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  thought to be contributing to the variability in stack opacity.

The principal mechanism considered responsible for increased  $\text{SO}_3$  formation in the boiler was the catalytic oxidation of sulfur dioxide ( $\text{SO}_2$ ) by iron oxide deposits on the fireside surface of the superheater tubes. These deposits, present as ash and/or scale, can reach temperatures that result in a high conversion rate of  $\text{SO}_2$  to  $\text{SO}_3$ . It was calculated that if the superheater were moderately fouled by deposits with a high catalytic activity, nearly 80 ppmv of  $\text{SO}_3$  could be forming in the superheater. The iron containing ash particles suspended in the flue gas, also expected to be catalytic, were not considered a substantial contributor to  $\text{SO}_3$  formation because the surface area of particles per unit of gas volume is small. There was a measured decline of approximately 20 ppmv in the  $\text{SO}_3$  concentration of the flue gas as its temperature dropped from 800 to 500 °F while it passed through the economizer and air heater. This temperature range is also associated with the reaction of  $\text{SO}_3$  with water vapor to form  $\text{H}_2\text{SO}_4$ . This  $\text{SO}_3$  reduction could not be attributed to a simple condensation process since the gas temperature of 500 °F was well above the dewpoint. It was concluded that the removal mechanism was adsorption of acid on the fly ash particles.

The concentration of acid mist present in the stack gas is the difference between the  $\text{SO}_3$  formed by catalytic oxidation of  $\text{SO}_2$  in the superheater and the amount of  $\text{H}_2\text{SO}_4$  adsorbed from the flue gas by the fly ash. Under the test conditions, 17 +/- 5 ppmv  $\text{SO}_3$  (actually  $\text{H}_2\text{SO}_4$ , reported as its equivalent in  $\text{SO}_3$ ) was measured entering the stack. An increase of only 10% (8 ppmv) in the amount of  $\text{SO}_3$  formed in the superheater, if not accompanied by an increase in the  $\text{H}_2\text{SO}_4$  adsorbed, would increase the average acid content of the flue gas by approximately 50%. The study conclusion was that the variability in plume opacity is due, first, to this sensitivity of acid emission, and second, to specific coal properties and combustion conditions.

The second case history to be discussed will focus on NYSEG's efforts to determine the cause of an intermittent detached brown plume which formed from the stack emissions of its A.E. Kintigh Station. Kintigh Station began operation in 1984 and has a generating capacity of 643 MW firing pulverized eastern bituminous coal. The plant is equipped with electrostatic precipitators and a wet limestone inhibited oxidation flue gas desulfurization (FGD) system. The scrubbed flue gas discharges to a wet stack with no reheat. Measurements of the flue gas constituents suggested that the plume could potentially be attributed to the presence of condensed  $\text{SO}_3$  leaving with scrubbed flue gas as fine acid mist particles. In an effort to reduce or eliminate the brown plume, a test program with ammonia injection into the flue gas prior to the precipitator was implemented. Ammonia injection was effective in reducing the  $\text{SO}_3$  vapor in the hot flue gas and also reduced the condensed particulate acid mist concentration and opacity of the cool flue gas. The program was believed to be successful, until during the last scheduled day of testing, a visible brown plume appeared and lasted for two hours. Conclusions of the test program were that some phenomenon other than  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  mist particulate was causing the brown appearance. Further studies attributed the brown appearance to the presence of certain local meteorological conditions in combination with an increase in the plume nitrogen dioxide ( $\text{NO}_2$ ) concentration, due to the oxidation of nitric oxide (NO) to  $\text{NO}_2$  by ambient ozone, as the flue gas was transported away from the stack.

NYSEG owns and operates two 150 MW pulverized bituminous coal fired boilers at Milliken Station. Each unit is equipped with an electrostatic precipitator and a wet limestone forced oxidation flue gas desulfurization system. Precipitator modifications and a flue gas desulfurization system were installed in 1993 and 1994 as part of the Department of Energy cofunded Milliken Station Clean Coal Technology Demonstration Project. While there is not an opacity or plume visibility issue at the Station, it is worth mentioning that flue gas analysis data suggests that as much as 15% of the SO<sub>3</sub> entering the FGD system is removed by the scrubbing process.